DMF in Acetic Anhydride: A Useful Reagent for Multiple-Component Syntheses of Merocyanine Dyes

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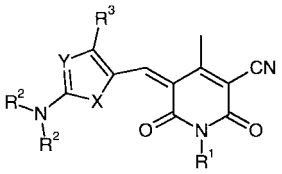
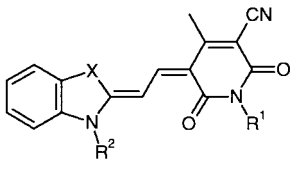
Abstract: A simple and highly efficient method for the preparation of merocyanine dyes is reported from mixtures of CH-acidic heterocycles and electron-rich dialkylaminothiazoles or methylene bases and various formylating reagents without isolation of the formylated intermediates. With the particularly useful formylation-condensation system of DMF in acetic anhydride and highly acidic 1,2,5,6-tetrahydro-2,6-dioxo-3-pyridinecarbonitriles **8**, the transformations could be carried out as multicomponent reactions to give pure dyes **3–6** in 50–90% yield directly from the reaction mixtures.

Key words: condensation, dyes, formylation, multicomponent reactions, nucleophiles, heterocycles, merocyanines

Polymethine dyes and their aza analogues have received considerable interest especially in the field of color photography because of their brilliant shades which are difficult to achieve with any other class of dyes.[1] However, their use in other fields like textile dyeing or many speciality applications is often prevented because of an inferior thermal, chemical, and photochemical stability compared to azo- or anthraquinone dyes. Also azo dye chemistry is based on efficient syntheses (in water!) and cheap starting materials whereas methine dye chemistry involves more expensive reactions like Vilsmeier formylations or orthoformate chemistry under anhydrous conditions.[2]



1: X = O, Y = CH
2: X = S, Y = CH
3: X = S, Y = N

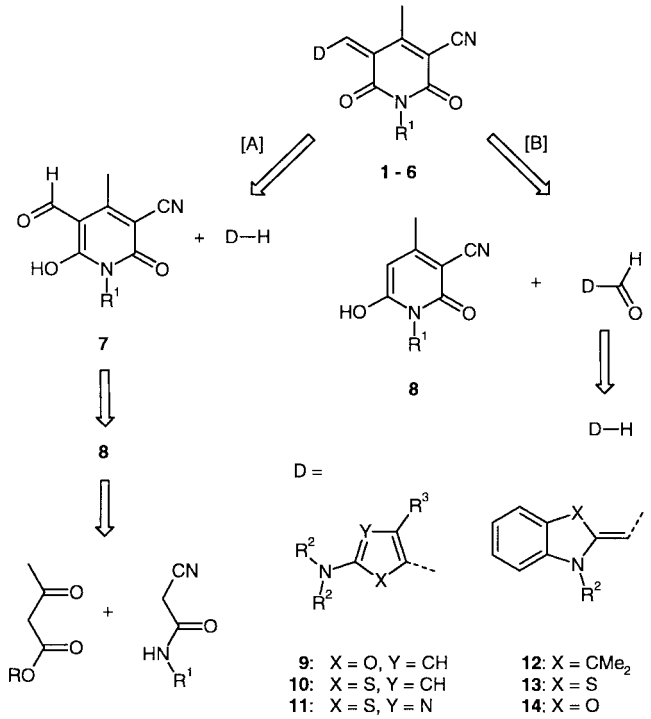


4: X = CMe_2
5: X = S
6: X = O

Recently, merocyanine dyes **1–6** were shown to exhibit a particularly promising chromogenic system for several high-technology applications.[3,4] First, only one electronic transition in the visible range with a cyanine-like narrow absorption band leads to very brilliant magenta hues suited for applications in digital photography and color copying.[5] Second, high dipole moments and polarizabilities in the direction of the conjugated chain enabled unprecedented refractive index modulations in photorefractive materials.[6] Third, based on their brilliancy and the recent observation of solid-state luminescence[4] especially bright colors on polyester were achieved which hold promise for textile coloration.[7] Moreover, the balanced electronic system of these chromophores with a bond-order of one and a half along the conjugated chain affords pretty high light fastness and thermal stabilities (onset of decomposition >250°C according to calorimetry).

Whereas the electronic system is an inherent property of the chromophore, each area of application has its own specific demands on the chemical and thermal stabilities, the wet and the light fastness as well as the solubility and the compatibility to polymeric binders. Due to a lack of rational guidelines these properties have to be optimized through extensive substituent variations and an application-directed screening protocol. The optimization process may be carried out in a traditional, i.e. sequential manner or by means of automated parallel synthesis as in the case of combinatorial chemistry.[8] Irrespective of the strategy, highly efficient reactions and screening methods are of primary importance if a promising chromophore has to be developed to a functional material which fulfills all requirements of the desired application. In this paper we describe such an easy and highly efficient synthesis of merocyanine dyes based on a multiple-component reaction involving a formylating reagent generated in situ from DMF in acetic anhydride.

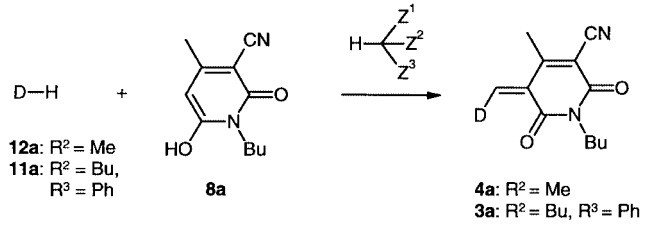
Scheme 1 shows the retrosynthetic analysis of the dye synthesis based on the easily accessible hydroxypyridones **8**,[9] thiazoles **11**,[10] and methylene bases **12–14**.[11,12] Whereas only two steps - a formylation and a condensation reaction - are required, the corresponding procedures are not convenient at all with respect to our goal of extensive variations of the substituents for the given applications. Lipophilic substituents R^1–R^5 as demanded for highly soluble dyes give high-boiling and viscous formylated intermediates which are difficult to isolate. If used as crude materials, however, lower yields and incomplete dye precipitation is often observed for the condensation reaction. Therefore we were looking for a more straightforward reaction sequence suited for a highly efficient synthesis of dyes **3–6** that exhibits a wide scope with regard to substituent variations for dyes of very different solubility properties. More specifically the reaction should be based on extremely simple procedures and laboratory equipment thus being applicable to automated parallel synthesis in simple test tubes (no dropping funnels, reflux condensors, etc.). This includes also the de-



Scheme 1

mand for an easy product isolation which disfavors any additional steps like chromatography or recrystallization.

A promising starting point was found in two papers of Hünig and Reidlinger et al. who prepared a number of merocyanine dyes directly from methylene bases and CH-acidic heterocyclic acceptors in the presence of formamide[13a] or triethyl orthoformate.[13b] Whereas both procedures are simple (however involving reflux conditions), the scope seems to be somewhat limited giving only high yields for special examples. Nevertheless we succeeded in preparing the indoline-based merocyanine dye **4a** under both reaction conditions (Table 1). With the orthoester method not only methylene bases like Fischer base **12a** could be used but also electron-rich dialkylaminothiazole **11a** (Table 1, Entries 2,3). For both examples, yields and purities were excellent. However, we encountered some problems when crude starting materials were used. In particular only one percent of water in the solvent (or in any of the other starting materials) resulted in significantly lower yields. For highly soluble dyes like **4e** (see below), no product could be precipitated out of the oily reaction mixture when only 99% ethanol was used.



This prompted us to study other common formic acid derivatives[14–16] in different solvents. Several of these reagents like *N*,*N*-dimethylchloromethylenminium chloride (Vilsmeier reagent) and dichloromethylmethylether gave fairly clean conversions to dyes **3a**, **4a**, but the isolation from DMF was not satisfactory giving microcrystalline precipitates of moderate purity which required time-consuming filtration and washing procedures (Table 1, Entries 4,5). Even more impure dyes were isolated from the reaction mixture of the common formylating reagent *N*,*N'*-diphenylformamidine in various solvents including DMF and acetic anhydride and almost no conversion to dyes **3a**,**4a** was observed for the more reactive formylating reagents dimethylformamide diethylacetal and bis(dimethylamino)-*tert*-butoxymethane ("Bredereck's reagent").[15] Finally, the ideal reagent was discovered in the little known formylating reagent DMF in acetic anhydride[17] which afforded yields and purities comparable to trialkyl orthoformates but was very tolerant towards crude starting materials (probably because nucleophilic impurities may react with an excess of the solvent) and allowed fast reactions at 90°C clearly below the boiling point of the mixture. For highly concentrated solutions of equimolar amounts of **8a** and **11a,12a**, and 1.5-fold amounts of a dialkylformamide derivative, almost quantitative conversions to merocyanine dyes **3a**,**4a** took place after about half an hour at 90°C. After 2 hours the mixtures were allowed to cool down to room temperature and pure crystalline solids could be isolated in a very simple manner by filtration and washing of the dyes with alcohol (Table 1, Entries 6–10).

Because morphological properties like compatibility to polymeric binders or the crystallization tendency[4] depend on the hardly predictable packing of the dyes in the solid state, an important aspect of our synthetic work was to find a method that offers a broad scope with respect to substituent variations. More specifically introduction of substituents having a high solubilizing power like long- and branched-chain alkyl groups and substituents with a high influence on packing properties like sterically demanding groups was desired.

Table 2 shows our results for reactions of several thiazoles **11a–c** and indolines **12a–d** with hydroxypyridones **8a–e**. The selected combinations provided dyes **3a–f** and **4a–h** that cover a solubility range of more than four orders of magnitude and melting points ranging from 100 to >330°C.[4] It is noteworthy that all yields given in Table 2 refer to the overall process of turnover, precipitation, and washing until analytically pure dyes could be isolated. Even with starting materials of a purity of only 70–90%, crystallization took place in fairly good yields from the reaction mixtures to afford pure dyes which exhibit only the single narrow and intense UV/Vis-absorption band that is characteristic for this chromophore.[3,4] Most important to our work, starting materials with sterically demanding substituents close to the reaction center could also be reacted (**3d–f**, **4d**,**f**,**h**). Here, the isolated yields are somewhat lower, which might be a consequence of an

Table 1 Isolated Yields[a] of Merocyanine Dyes **3a** and **4a** with Different Formylating Reagents (General Procedure A)

Entry	Dye	Formylating Reagent (equiv)[b]	Solvent (equiv)[c]	Temp/Time (h)	Yield (%)
1	**4a**	$HCONH_2$ (25)	–	130°C/8	20
2	**3a**	$HC(OMe)_3$ (1.5)	EtOH (10)	90°C/1	85
3	**4a**	$HC(OEt)_3$ (1.5)	EtOH (10)	90°C/2	80
4	**3a**	Cl_2CHOMe (1.5)	DMF (5)	90°C/5	40[d]
5	**3a**	Cl_2CHNMe_2 (1.5)	DMF (5)	100°C/2	45[d]
6	**4a**	DMF (1.5)	Ac_2O (4.5)	40°C/10	40
7	**3a**	DMF (1.5)	Ac_2O (4.5)	90°C/2	85
8	**4a**	DMF (1.5)	Ac_2O (4.5)	90°C/2	85
9	**3a**	*N*-FP (1.5)	Ac_2O (4.5)	90°C/2	85
10	**3a**	*N*-MFA (1.5)	Ac_2O (4.5)	90°C/2	60
11	**3a**	DMF (4)	AcCl (2)	100°C/3	72

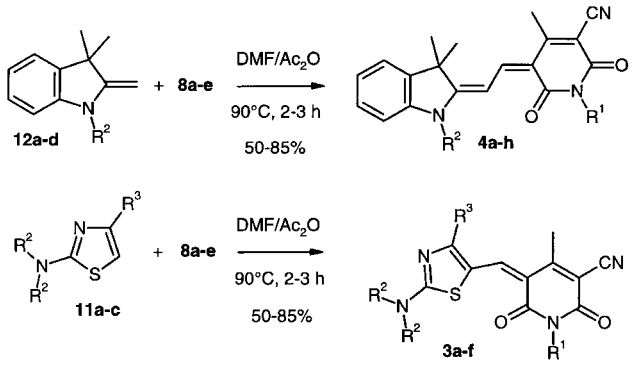
[a] Yields of >90% pure dyes as isolated from the reaction mixture after washing with *i*-PrOH.
[b] Molar amounts of the formylating reagent; *N*-FP = *N*-formylpiperidine, *N*-MFA = *N*-methylformanilide, Cl_2CHNMe_2 = $[ClCHNMe_2]^+Cl^-$ (Vilsmeier reagent).
[c] Molar amount of the solvent.
[d] Dye precipitation after addition of water.

Table 2 Merocyanine Dyes **3b–f** and **4b–h** Prepared (General Procedure B)

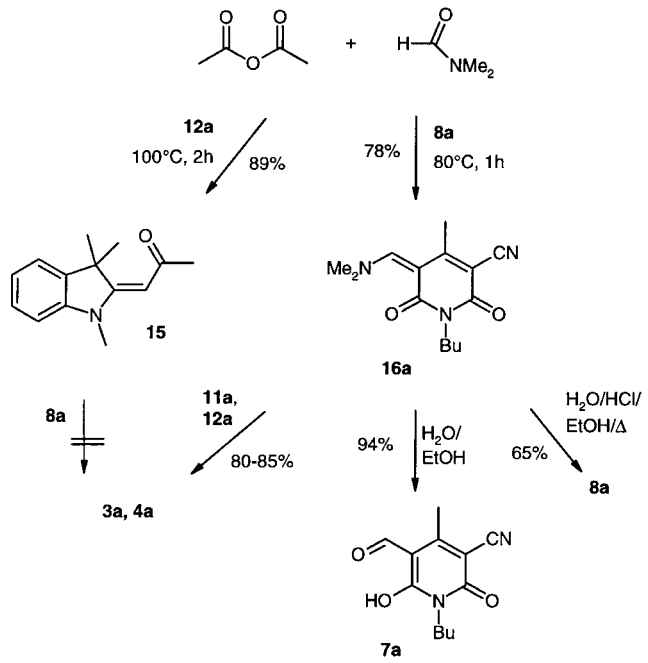
Starting Materials	Dye	R^1	R^2	R^3	Yield[a] (%)
8b,11a	**3b**	Me	Bu	Ph	85
8d,11a	**3c**	Hex	Bu	Ph	75
8b,11b	**3d**	Me	Bu	*t*-Bu	60
8a,11b	**3e**	Bu	Bu	*t*-Bu	50
8b,11c	**3f**	Me	Et	Neopentyl	60
8b,12a	**4b**	Me	Me	–	85
8a,12b	**4c**	Bu	Pr	–	70
8a,12c	**4d**	Bu	*i*-Pr	–	60
8a,12d	**4e**	Bu	Bu	–	70
8d,12c	**4f**	Hex	*i*-Pr	–	50
8c,12d	**4g**	Pentyl	Bu	–	70
8e,12c	**4h**	2-Ethex[c]	*i*-Pr	–	80[b]

[a] Yields of pure dyes as isolated from the reaction mixture after washing with *i*-PrOH and/or EtOH/H_2O.
[b] Isolated by chromatography.
[c] 2-Ethylhexyl.

incomplete precipitation caused by the increased solublity of these dyes.



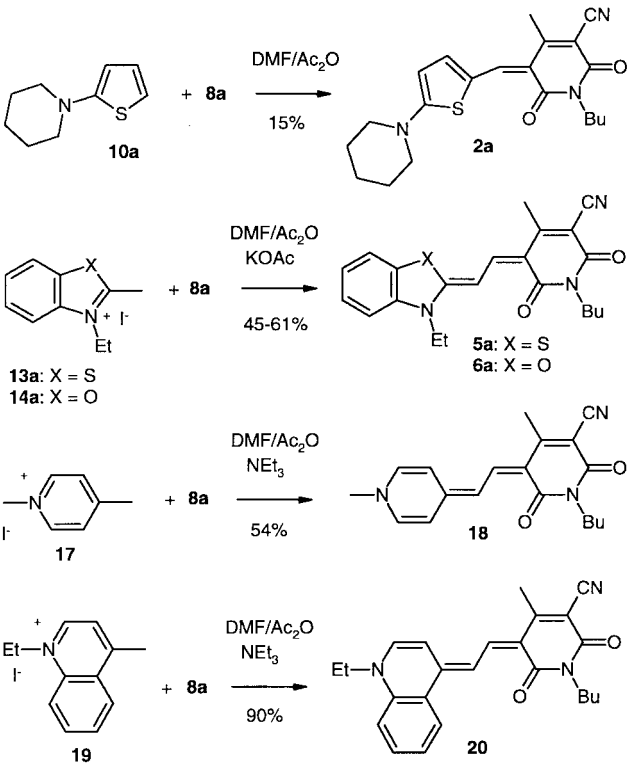
For a mechanistic understanding we investigated the reaction of the single components **8a**, **11a** and **12a** with DMF in acetic anhydride at 80–100°C (Scheme 2). No reaction was observed for thiazole **11a** under these conditions



Scheme 2

while the other two nucleophiles reacted completely within 2 hours. However, after addition of the second reactant to the mixtures, dye formation was only observed from the intermediate obtained from hydroxypyridone **8a**. Here both dyes **3a** and **4a** could be obtained in rather exothermic reactions and the yields were comparable to those given in Table 1 for the multicomponent reactions. It was also possible to isolate the intermediate enamine **16a** in good yields under strictly anhydrous conditions. Otherwise, in the presence of water immediate hydrolysis of the highly reactive enamine **16a** takes place to give the formylated pyridone **7a** (as already observed in NMR experiments in $CDCl_3$ or DMSO-d_6 at very low water contents). Under more severe conditions even deformylation to the starting material **8a** was observed. On the other hand, the unreactive intermediate which could be isolated in high yield from the reaction mixture of the methylene base **12a**, DMF and acetic anhydride, was shown to be the acetylated derivative **15**[18a,b] instead of the expected formylation product. DMF is not crucial for this acetylation which also takes place in pure acetic anhydride at temperatures above 60°C and requires about 5 hours at 70°C or 1.5 hours at 90°C for >95% conversion. We therefore conclude that the reaction sequence leading to dyes **3** and **4** involves an *O*-acylation of the dialkylformamide by acetic anhydride to a Vilsmeier-type reagent as proposed by Eiden,[17] which is sufficiently reactive to formylate the highly nucleophilic hydroxypyridones **8** to yield enamines **16**. In the presence of electron-rich methylene bases **11** or heterocycles **12**, subsequent acetic anhydride promoted condensations take place instantaneously to give merocyanine dyes **3** and **4** in almost quantitative yields. This mechanistic understanding is also supported by the possibility to use acetyl chloride instead of acetic anhydride for the activation of DMF (Table 1, Entry 11).

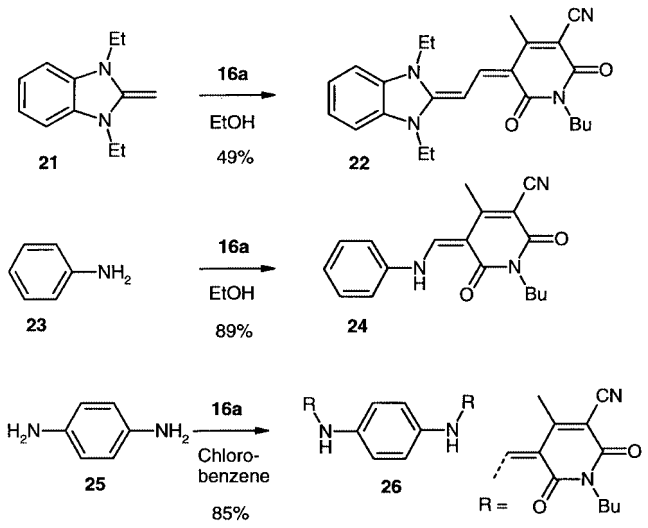
To elucidate the scope of this one-pot procedure we performed reactions with a number of electron–rich aromatics and methylene bases as well as CH-acidic acceptor heterocycles. The variations of the electron-donating unit in the dyes included dimethylaniline, julolidine, thiophene **10a** and several methylene bases (**13**, **14**, **17**, **19**). The less nucleophilic aromatics failed to give the desired merocyanines and thiophene **10a** afforded only a low yield of dye **2a**, however, benzoxazole and benzothiazole dyes **5a**,**6a** could be prepared in remarkable yields from the in situ generated methylene bases. This variation of the reaction conditions was advantagous because of the high reactivity of these more nucleophilic methylene bases towards acetylation and the easy availability of the iodide salts **13a** and **14a**. No attempts were made with respect to an optimization of the base.



Unlike the compounds described above, the even more nucleophilic methylene bases of 1,4-dimethylpyridinium (**17**) and 1-ethyl-4-methylquinolinium (**19**) iodide could not be reacted in a multicomponent fashion. Therefore stepwise reactions were carried out, first converting the pyridone to the enamine and then adding the heterocyclic iodide salts and one equivalent of a base. With potassium acetate the yield of **18** was only 20%, but with triethylamine 54% of pure pyridine dye **18** and 90% of quinoline dye **20** could be isolated directly from the reaction mix-

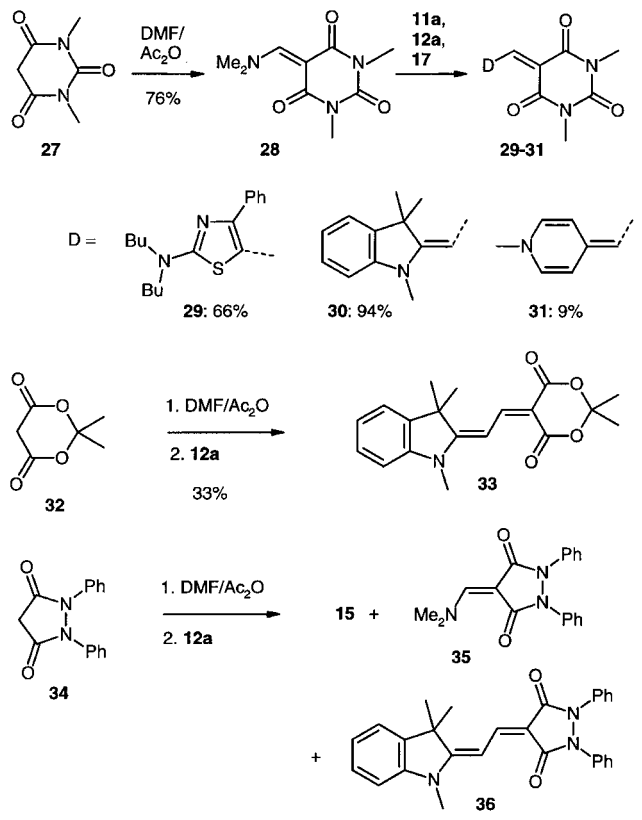
ture. The stronger base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded comparable yields.

Alternatively highly reactive nucleophiles **21**,**23**,**25** which are prone to acetylation in acetic anhydride[19] could be reacted with enamine **16a** in inert solvents to give another series of dyes **22**,**24**,**26** in moderate to high yields. In contrast to the former dyes, which exhibit magenta and violet hues, these chromophores are characterized by yellow and orange colors and very interesting solid-state luminescence properties.

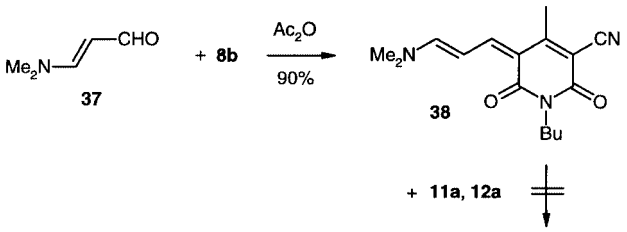


After studying methine bond formation between enamine **16a** and donor bases of different nucleophilicity, variations of the CH-acidic acceptor heterocycles were investigated. The reactions were carried out with the following substrates: 1,3-indanedione, dioxopyrazole **34**, Meldrum's acid **32** and barbituric acid **(27)**. In all cases the respective enamines were formed at 90°C, but their reactivity was significantly reduced compared to **16a** (decreasing in the order **8** > **27** > **32** > **34** > indandione).[20] Only the reaction between barbituric acid, DMF and the less nucleophilic thiazole base **11a** gave a satisfactory yield of 40% of pure dye **29** in the multicomponent synthesis, whereas the more reactive indoline **12a** reacted partly to **15** giving an isolated yield of only 3% of dye **30**. However, from the in situ generated enamines of the six-membered heterocycles **32** and **27**, thiazole as well as indoline dyes are obtained in satisfactory yields. Attempts to react the even less electrophilic enamines of the five-membered heterocycles were not successful because of the predominant acetylation of the methylene base. Thus the product isolated by precipitation from the reaction mixture of **34** and **12a** was a mixture of enamine **35** (60 mol%) and dye **36** (40 mol%), whereas the acetylated methylene base **15** remained in solution.

For the same reason our attempts to synthesize tri- and tetramethine dyes according to the vinylogic principle have not been successful. Although the reaction with acrolein



37 took place in a high yield, the yellow dye **38** proved to be stable and rather unreactive in contrast to the highly electrophilic lower homologue **16a**.



Finally it is noteworthy that all of the chromophores described in this work are very brilliant dyestuffs as desired for printing applications. This brilliancy is related to an electronic structure with almost identical contributions of the unpolar and the zwitterionic resonance structures for both the ground and the excited states.[3,21] For this special electron distribution there is no dipole change and almost no change in the nuclear coordinates of the dyes and no reorientation of the surrounding solvent molecules upon optical excitation. As a result the dye exhibits only one strongly allowed electronic transition from the S_0 to the S_1 electronic state with a most intense vibrational 0,0-transition affording very intense and narrow absorption bands (half width $\Delta\nu_{1/2} = 900–1500\ cm^{-1}$) and brillant hues which are otherwise only observed for the symmetric cationic cyanine or anionic oxonole dyes. As an example the

absorption spectra of three selected dyestuffs of our series which form a nice trichromatic system of the primary colors yellow (**30**, λ_{max} = 466 nm), magenta (**3f**, λ_{max} = 526 nm) and cyan (**20**, λ_{max} = 617 nm) are displayed in the figure.

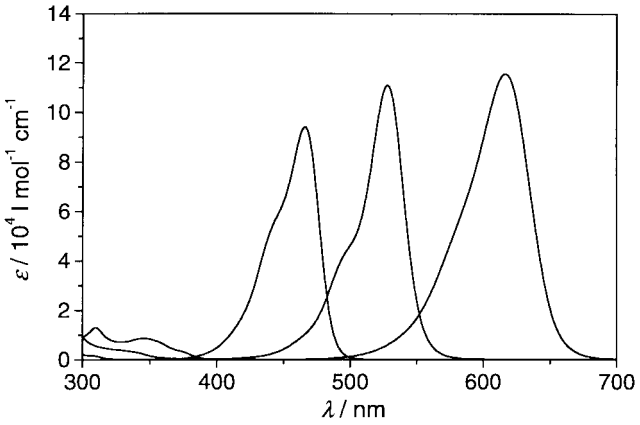


Figure UV/VIS absorption spectra of a trichromatic system based on the yellow indoline dye **30** (left), the magenta thiazole dye **3f** (middle) and the blue quinoline dye **20** (right) in dichloromethane.

In conclusion we have described very efficient one-pot procedures for the preparation of merocyanine dyes based on a simple formylating reagent derived from DMF in acetic anhydride. The reactions proceed through reactive enamines of the CH-acidic heterocycles **8**, **32**, **27** and a subsequent condensation with the electron-rich heterocycles **10**, **11** or methylene bases **12–14**,**17**,**19**. For the most valuable magenta dyes **3–6** the reactions could be carried out in high yields and purities in a multicomponent fashion by simply mixing all reactants together for 2 hours at 90°C and washing the precipitated dye with alcohol/water. It is interesting that this convenient one-step procedure was applicable exactly to those dyes which are characterized by equal contributions of the nonpolar and the zwitterionic resonance structures (merocyanines in the "cyanine limit")[3,21a] which are highly desired for electrooptic materials, digital printing technologies and polyester dyeing.[3,4,7]

^{1}H NMR spectra were recorded at r.t. on Bruker instruments at 200 and 500 MHz. Chemical shifts (δ) are given in ppm downfield from TMS as internal standard. All dialkylamino substituents of the thiazole dyes **3a–f** show characteristic broad signals (br s) due to hindered rotation around the N–$C_{thiazole}$ bond. EI mass spectra (70 eV) were recorded using a Finnigan MAT SSQ 7000 spectrometer. UV/VIS absorption spectra were measured on a Perkin Elmer Lambda 40P instrument from 230–800 nm in CH_2Cl_2 (Merck Uvasol). Absorption maxima λ_{max} and extinction coefficients ε_{max} are given in nm and $Lmol^{-1}cm^{-1}$. All melting points were determined with a Büchi SMP 20 instrument with a heating rate of 2°C/min and are uncorrected. For HPLC measurements a Merck-Hitachi system (pump L-6200A, UV detector L-4000) and a Merck LiChroCart 250-4 column packed with LiChrospher Si 60 (5 μm) was used.

Starting materials were prepared according to the literature and were typically used in crude form (at a purity of 70–95% according to GC or ^{1}H NMR analysis): 1-alkyl-4-methyl-2,6-dioxo-1,2,3,6-tetrahydro-pyridine-3-carbonitriles **8a–e**,[9] 2-dialkylamino-4-substituted thiazoles **11a–c**,[10] 1-alkyl-3,3-dimethyl-2-methylene-indolines **12a–d**,[11a], 2-piperidinothiophene **(10a)**.[12a] DMF, EtOH and MeOH were dried according to known procedures.[22] All other solvents were used without further purification and reactions were carried out without protection from moisture or oxygen unless specific details are given in the text. The dyes were dried in vacuo at 50–60°C for 1 d. Spectral and physical data of all the compounds prepared are given in Table 3.

Multicomponent Reactions Using Various Formylating Reagents; General Procedure A (Table 1)

Equimolar amounts of indoline **12a** (or thiazole **11a**) and pyridone **8a** were mixed in the solvent given in Table 1 by stirring. The formylating reagent was added and the mixture was heated according to the conditions given in Table 1. After the reaction was complete (TLC control) the mixtures were allowed to cool to r.t., stirred for 2–18 h and the precipitated dyes were collected and washed with *i*-PrOH until the color of the filtrate changed from violet to pink (**3a**) or pale orange (**4a**). The dyes were dried at 60°C in vacuo and the purity was controlled by HPLC to be at least 90% for all reactions given in Table 1.

Multicomponent Reactions Using DMF in Acetic Anhydride; General Procedure B, for Dyes 3a–f, 4a–h (Table 2) and 2a

To a mixture of equimolar amounts of a thiazole **11a–c** or an indoline **12a–d** and a pyridone **8a–e**, a 1.5-fold molar amount of DMF and a 4–5-fold molar amount of Ac_2O were added and the mixture was heated at a bath temperature of 90°C for 2–3 h. The mixture was allowed to cool to r.t. and stirring was continued for 2–18 h. The precipitated dye was collected on a Büchner funnel, washed thoroughly with *i*-PrOH (or EtOH/H_2O for more soluble derivatives) until the color of the filtrate changed from violet to pink (**3**) or orange (**4**). After drying at 60°C in vacuo dyes of a purity of 96–100% are obtained based on spectroscopy (NMR, UV/VIS) and elemental analyses.

1-Butyl-5-(2-dibutylamino-4-phenylthiazol-5-ylmethylene)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (3a)

From **11a** (14.4 g, 0.05 mol), **8a** (10.3 g, 0.05 mol) and DMF (5.5 g, 0.075 mol) in Ac_2O (25 mL, 0.25 mol). After cooling to r.t., the precipitated dye was filtered, washed with *i*-PrOH (3 × 20 mL) and dried to give 19–20 g (80–85%) of green needles.

1-Butyl-5-[2-(1,3-dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)ethylidene]- 4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (4a)

From **12a** (8.65 g, 0.05 mol), **8a** (10.3 g, 0.05 mol) and DMF (5.5 g, 0.075 mol) in Ac_2O (25 mL, 0.25 mol). After cooling to r.t., the precipitate was filtered, washed with *i*-PrOH (3 × 20 mL) and dried to give 16.5 g (85%) of a pink solid. Recrystallization from toluene gave red leaflets.

1-Butyl-5-[2-(1,3-dihydro-3,3-dimethyl-1-propyl-2*H*-indol-2-ylidene)ethylidene]-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (4c)

Reaction was carried out as described for **4a** starting from **12b** (2.0 g, 0.01 mol), **8a** (2.06 g, 0.01 mol) and DMF (1.1 ml, 0.015 mol) in Ac_2O (5 mL). Because of the good solubility, precipitation was completed in an ice–bath and Et_2O and EtOH/H_2O (7:3) were used for the washing procedure, giving 2.9 g (70%) of a red solid.

Table 3 Spectroscopic and Physical Data of Dyes Prepared[a,b]

Dye	mp (°C)	UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm ($Lmol^{-1}cm^{-1}$)]	^1H NMR (200 MHz, $CDCl_3$/TMS) δ, *J* (Hz)[c]
3a	175	536 (89000)	7.77 (s, 1 H, met-H), 7.45–7.7 (m, 5 H, Ph-H), 3.98 (t, 2 H, *J* = 7, NCH_2), 3.8 (br s, 2 H, NCH_2), 3.5 (br s, 2 H, NCH_2), 2.20 (s, 3 H, CH_3), 1.2–1.8 (m, 12 H, CH_2), 0.9–1.1 (m, 9 H, CH_3)
3f	242	526 (118000)	7.86 (s, 1 H, met-H), 3.7 (br s, 4 H, NCH_2), 3.34 (s, 3 H, NCH_3), 2.84 (s, 2 H, CH_2), 2.55 (s, 3 H, CH_3), 1.35 (br s, 6 H, CH_3), 1.04 (s, 9 H, *t*-C_4H_9)
4a	250	522 (135000)	7.99 (AB, 2 H, *J* = 14, met-H), 7.1–7.5 (m, 4 H, ar-H), 3.99 (t, 2 H, *J* = 8, NCH_2), 3.64 (s, 3 H, NCH_3), 2.53 (s, 3 H, CH_3), 1.73 (s, 6 H, CH_3), 1.62 (m_c, 2 H, CH_2), 1.41 (m_c, 2 H, CH_2), 0.94 (t, 3 H, *J* = 7, CH_3)
4c	193	527 (130000)	8.02 (AB, 2 H, *J* = 14, met-H), 7.35–7.45 (m, 2 H, ar-H), 7.20–7.30 (m, 1 H, ar-H), 7.08 (m_c, 1 H, ar-H), 4.04 (t, 2 H, *J* = 7, NCH_2), 3.99 (t, 2 H, *J* = 7, NCH_2), 2.51 (s, 3 H, CH_3), 1.93 (m_c, 2 H, *J* = 7, CH_2), 1.72 (s, 6 H, CH_3), 1.62 (m_c, 2 H, CH_2), 1.41 (m_c, 2 H, CH_2), 1.06 (t, 3 H, *J* = 7, CH_3), 0.94 (t, 3 H, *J* = 7, CH_3)
4f	185–186		8.09 (AB, 2 H, *J* = 14, met-H), 7.15–7.45 (m, 4 H, ar-H), 4.87 (m_c, 1 H, NCH), 3.98 (t, 2 H, *J* = 8, NCH_2), 2.52 (s, 3 H, CH_3), 1.71 (s, 6 H, CH_3), 1.69 (d, 6 H, CH_3), 1.64 (m_c, 2 H, CH_2), 1.33 (m_c, 6 H, CH_2), 0.88 (t, 3 H, *J* = 7, CH_3)
4g	185–187		8.03 (AB, 2 H, met-H), 7.10 – 7.45 (m, 4 H, ar-H), 4.07 (t, 2 H, *J* = 7, NCH_2), 3.97 (t, 2 H, *J* = 7, NCH_2), 2.52 (s, 3 H, CH_3), 1.2 – 2.0 (m, 10 H, CH_2), 1.72 (s, 6 H, CH_3), 1.01 (t, 3 H, *J* = 7, CH_3), 0.89 (t, 3 H, *J* = 7, CH_3)
4h	158		8.08 (AB, 2 H, met-H), 7.2–7.4 (m, 4 H, ar-H), 4.86 (m_c, 1 H, NCH), 3.92 (m_c, 2 H, NCH_2), 2.52 (s, 3 H, CH_3), 1.90 (m_c, 1 H, CH), 1.71 (s, 6 H, CH_3), 1.68 (d, 6 H, *J* = 6, CH_3), 1.31 (m_c, 8 H, CH_2), 0.90 (m_c, 6 H, CH_3)
2a	235	538 (157000)	7.50 (m_c, 2 H, thio-H4, met-H), 6.44 (d, 1 H, *J* = 5, thio–H3), 3.97 (t, 2 H, *J* = 7, NCH_2), 3.67 (br s, 4 H, pip–NCH_2), 2.46 (s, 3 H, CH_3), 1.79 (br s, 6 H, pip–CH_2), 1.66 (m_c, 2 H, CH_2), 1.41 (m_c, 2 H, CH_2), 0.94 (t, 3 H, *J* = 7, CH_3)
5a	312	533 (137000)	500 MHz: 8.07 (d, 1 H, *J* = 13, met-H), 7.77 (d, 1 H, *J* = 13, met-H), 7.69 (d, 1 H, *J* = 8, ar-H), 7.54 (t, 1 H, *J* = 8, ar-H), 7.40 (m, 2 H, ar-H), 4.37 (q, 2 H, *J* = 7, NCH_2), 3.99 (t, 2 H, *J* = 8, NCH_2), 2.52 (s, 3 H, CH_3), 1.63 (m_c, 2 H, CH_2), 1.55 (m_c, 3 H, CH_3), 1.40 (m_c, 2 H, CH_2), 0.95 (t, 3 H, *J* = 7, CH_3)
6a	284–288	495 (145000)	500 MHz: 8.14 (d, 1 H, *J* = 14, met-H), 7.62 (d, 1 H, *J* = 14, met-H), 7.55 (m, 1 H, ar-H), 7.42 (m, 2 H, ar-H), 7.30 (m, 1 H,ar-H), 4.22 (q, 2 H, *J* = 7, NCH_2), 3.99 (t, 2 H, *J* = 7, NCH_2), 2.55 (s, 3 H, CH_3), 1.62 (m_c, 2 H, CH_2), 1.55 (t, 3 H, *J* = 7, CH_3), 1.40 (m_c, 2 H, CH_2), 0.95 (t, 3 H, *J* = 7, CH_3)
18	290–294	550 (110000)	DMSO-d_6: 8.40 (d, 2 H, *J* = 7, pyr-H), 7.70–7.90 (m, 4 H, pyr-H, met-H), 4.07 (s, 3 H, NCH_3), 3.82 (t, 2 H, *J* = 7, NCH_2), 2.42 (s, 3 H, CH_3), 1.46 (m_c, 2 H, CH_2), 1.30 (m_c, 2 H, CH_2), 0.90 (t, 3 H, *J* = 7, CH_3)
20	285–287	617 (116000)	500 MHz in DMSO-d_6: 8.73 (d, 1 H, *J* = 14, met-H), 8.70 (d, 1 H, *J* = 7, quin-H), 8.45 (d, 1 H, *J* = 9, quin-H), 8.23 (d, 1 H, *J* = 9, quin-H), 8.07 (d, 1 H, *J* = 7, quin-H), 8.05 (m_c, 1 H, quin-H), 8.03 (d, 1 H, *J* = 14, met-H), 7.85 (t, 1 H, *J* = 8, quin-H), 4.73 (q, 2 H, *J* = 7, NCH_2), 3.86 (t, 2 H, *J* = 7, NCH_2), 2.50 (s, 3 H, CH_3), 1.48 (m_c, 5 H, CH_2,CH_3), 1.28 (m_c, 2 H, CH_2), 0.90 (t, 3 H, *J* = 7, CH_3)
22	282–283	471 (69000)	7.93 (d, 1 H, *J* = 15, met-H), 7.55 (s, 4 H, ar-H), 7.48 (d, 1 H, *J* = 14, met-H), 4.46 (q, 4 H, *J* = 7, NCH_2), 4.01 (t, 2 H, *J* = 7, NCH_2), 2.42 (s, 3 H, CH_3), 1.65 (t, 6 H, *J* = 7, CH_3), 1.5–1.7 (m, 2 H, CH_2), 1.3–1.5 (m, 2 H, CH_2), 0.92 (t, 3 H, *J* = 7, CH_3)
24	203–204		13.1 (br d, 1 H, *J* = 13, NH), 8.25 (d, 1 H, *J* = 13, met-H), 7.49 (m_c, 2 H, ar-H), 7.33 (m_c, 3 H, ar-H), 3.98 (t, 2 H, *J* = 7, NCH_2), 2.54 (s, 3 H, CH_3), 1.61 (m_c, 2 H, CH_2), 1.39 (m_c, 2 H, CH_2), 0.95 (t, 3 H, *J* = 7, CH_3)
26	330–335 (dec)		500 MHz in DMSO-d_6 at 120°C: 12.9 (br s, 2 H, NH), 8.52 (s, 2 H, met-H), 7.69 (s, 4 H, ar-H), 3.92 (t, 4 H, *J* = 7, NCH_2), 2.55 (s, 6 H, CH_3), 1.58 (m_c, 4 H, CH_2), 1.33 (m_c, 4 H, CH_2), 0.92 (t, 6 H, *J* = 7, CH_3)

Table 3 (continued)

Dye	mp (°C)	UV/VIS (CH_2Cl_2) λ_{max} (ε) [nm ($Lmol^{-1}cm^{-1}$)]	^1H NMR (200 MHz, $CDCl_3$/TMS) δ, *J* (Hz)[c]
29	180–181		8.55 (s, 1 H, met-H), 7.63 (m_c, 2 H, ar-H), 7.52 (m_c, 3 H, ar-H), 3.7 (br s, 4 H, NCH_2), 3.38 (s, 3 H, NCH_3), 3.33 (s, 3 H, NCH_3), 1.70 (m_c, 4 H, CH_2), 1.40 (m_c, 4 H, CH_2), 0.99 (t, 6 H, *J* = 7, CH_3)
30	315	466 (93000)	DMSO-d_6: 8.53 (d, 1 H, *J* = 15, met-H), 7.57 (m_c, 1 H, ar-H), 7.48 (d, 1 H, *J* = 15, ar-H), 7.38 (m_c, 2 H, ar-H), 7.25 (m_c, 1 H, ar-H), 3.54 (s, 3 H, NCH_3), 3.19 (s, 3 H, NCH_3), 3.17 (s, 3 H, NCH_3), 1.63 (s, 6 H, CH_3)
31	>310	505 (104000)	DMSO-d_6: 8.06–8.12 (m, 3 H, pyr-H, met-H), 7.42 (d, 2 H, *J* = 6, pyr-H), 7.38 (d, 1 H, *J* = 15, met-H), 3.93 (s, 3 H, NCH_3), 3.14 (s, 6 H, NCH_3)
33	235–238[d]	450 (68000)	8.63 (d, 1 H, *J* = 14, met-H), 7.15–7.45 (m, 4 H, ar-H, met-H), 7.00–7.08 (m, 1 H, ar-H), 3.53 (s, 3 H, NCH_3), 1.73 (s, 6 H, CH_3)
38	265–270 (dec)	462 (106000)	7.25–7.60 (m, 3 H, met-H), 3.96 (t, 2 H, *J* = 7, NCH_2), 3.37 (s, 3 H, NCH_3), 3.23 (s, 3 H, NCH_3), 2.39 (s, 3 H, CH_3), 1.58 (m_c, 2 H, CH_2), 1.39 (m_c, 2 H, CH_2), 0.93 (t, 3 H, *J* = 7, CH_3)

[a] Spectroscopic data for thiazole dyes **3b-e** and indoline dyes **4b**, **4d-f** are given in Lit.[4]
[b] Satisfactory elemental analyses were obtained for all dyes: C ± 0.28, H ± 0.17, N ± 0.17, S ± 0.20.
[c] br s = broad signal, met = methine, thio = thiophene, pip = piperidyl, pyr = pyridine, quin = quinoline.
[d] Lit.[25] mp 232–235°C.

1-Hexyl-5-[2-(1,3-dihydro-3,3-dimethyl-1-isopropyl-2*H*-indol-2-ylidene)ethylidene]-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (4f)

Reaction was carried out as described for **4c** starting from from **8d** (2.34 g, 0.01 mol), **12c** (2.0 g, 0.01 mol) and DMF (1.1 mL, 0.015 mol) to give a pink solid in 50% yield. Recrystallization from toluene/hexane gave red crystals.

5-[2-(1-Butyl-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene)ethylidene]-2,6-dioxo-1-pentyl-1,2,5,6-tetrahydropyridine-3-carbonitrile (4g)

Reaction was carried out as described for **4c** from **12d** (2.68 g, 0.01 mol of 80% purity), **8c** (2.20 g, 0.01 mol) and DMF (1.1 g, 0.015 mol) in Ac_2O (5 mL) to give 3.1 g (70%) of a pink solid which was recrystallized from toluene to yield 2.3 g of violet needles.

1-(2-Ethylhexyl)-5-[2-(1,3-dihydro-1-isopropyl-3,3-dimethyl-2*H*-indol-2-ylidene)ethylidene]-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (4h)

Reaction was carried out as described for **4a** starting from **8e** (2.62 g, 0.01 mol), **12c** (2.0 g, 0.01 mol) and DMF (1.1 mL, 0.015 mol). After cooling, a dark red solution was obtained. This mixture was concentrated to give an oily residue which was purified by column chromatography on silica gel using CH_2Cl_2/MeOH (97:3) as eluent. After evaporation of the solvent an oil was obtained which crystallized in the refrigerator after several days to give a pink solid in 80% yield which could be recrystallized from EtOH.

1-Butyl-4-methyl-2,6-dioxo-5-(2-piperidinothiophen-5-ylmethylene)-1,2,5,6-tetrahydropyridine-3-carbonitrile (2a)

From **10a** (1.7 g, 0.01 mol), **8a** (2.1 g, 0.01 mol) and DMF (1.1 g, 0.0015 mol) in Ac_2O (3.7 mL, 0.035 mol). After cooling to r.t., the precipitate was filtered, washed with *i*-PrOH (3 × 4 mL), recrystallized from toluene and dried to give 0.6 g (15%) of green needles.

1-(1,3-Dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)propan-2-one (15)

A mixture of **12a** (3.46 g, 0.02 mol), DMF (2.20 g, 0.03 mol) and Ac_2O (8 mL) was heated at 100°C for 2 h till all the starting material had disappered according to TLC control (silica gel; toluene/EtOAc, 9:1). After cooling to r.t., EtOAc (20 mL) was added and the organic phase was washed with brine and aq 2 N NaOH until a pH of 9 was reached. The organic layer was washed once more with brine, dried (Na_2SO_4), filtered and concentrated to give 4.0 g of a red oil. Column chromatography on silica gel with toluene/EtOAc (9:1) as eluent afforded a yellowish solid which was recrystallized from cyclohexane to give 3.83 g (89%) of pale yellow crystals; mp 98°C (Lit.[2b] mp 98–99°C).

^1H NMR (200 MHz, $CDCl_3$): two isomers in a 9:1 ratio: δ = 7.10–7.25 (m, 2 H, ar-H), 6.80–7.00 (m, 1 H, ar-H), 6.72 (d, 1 H, *J* = 8 Hz, ar-H), 5.30 (s, 0.9 H, met-H), 5.17 (s, 0.1 H, met-H), 3.58 (s, 0.3 H, NCH_3), 3.16 (s, 2.7 H, NCH_3), 2.20 (s, 0.3 H, acetyl-H), 2.18 (s, 2.7 H, acetyl-H), 1.78 (s, 0.6 H, CH_3), 1.72 (s, 5.4 H, CH_3).

MS (EI): *m*/*z* (%) = 215 (100), 199 (97).

1-Butyl-4-methyl-5-dimethylaminomethylene-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (16a)

A mixture of **8a** (10.3 g, 0.05 mol), DMF (5.5 g, 0.075 mol) and Ac_2O (25 mL) was heated at 80–90°C for 1 h. Upon cooling to r.t. **16a** precipitated. Filtration and washing with cold Ac_2O and absolute Et_2O afforded a cream-white solid which was dried to yield 10.2 g (78%) of **8a**; mp 185–190°C (dec).

^1H NMR (200 MHz, $CDCl_3$): δ = 7.76 (s, 1 H, met-H), 3.93 (t, 2 H, *J* = 7 Hz, NCH_2), 3.53 (s, 3 H, NCH_3), 3.27 (s, 3 H, NCH_3), 2.39 (s, 3 H, CH_3), 1.56 (m_c, 2 H, CH_2), 1.36 (m_c, 2 H, CH_2), 0.92 (t, 3 H, *J* = 7 Hz, CH_3).

MS (EI): *m*/*z* (%) = 261 (45), 244 (79), 190 (100).

Anal. calcd for $C_{14}H_{19}N_3O_2$ (261.3): C, 64.35; H, 7.33; N, 16.08. Found C, 64.11; H, 7.30; N, 15.85.

1-Butyl-5-formyl-6-hydroxy-4-methyl-2-oxo-1,2-dihydropyridine-3-carbonitrile (7a)

Compound **16a** (1.30 g, 0.005 mol) was suspended in 96% EtOH (40 mL) and stirred at r.t. After addition of H_2O (10 mL), the solid

dissolved and the solution turned red. After 30 min additional amount of H_2O (30 mL) was added and the solution was concentrated. 1 N HCl (ca 4 mL) was added until a pH of 1 was reached and a cream-white solid precipitated, which turned a little brownish during drying at 40°C in vacuo to give 1.1 g (94%) of **7a**, which was >95% pure according to NMR. Sublimation afforded a white solid; mp 98°C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.83 (s, 1 H, CHO), 4.01 (t, 2 H, *J* = 7 Hz, NCH_2), 2.53 (s, 3 H, CH_3), 1.63 (m_c, 2 H, CH_2), 1.39 (m_c, 2 H, CH_2), 0.95 (t, 3 H, *J* = 7 Hz, CH_3).

MS (EI, 70eV): *m*/*z* (%) = 234 (28), 217 (100), 192 (49), 179 (88), 150 (48).

Anal. calcd $C_{12}H_{14}N_2O_3$ (234.3): C, 61.53; H, 6.02; N, 11.96. Found C, 61.70; H, 5.99; N, 11.82.

1-Butyl-5-[2-(3-ethyl-3*H*-benzothiazol-2-ylidene)ethylidene]-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (5a); Typical Procedure

A mixture of **13a** (0.92 g, 3 mmol), **8a** (0.62 g, 3 mmol), DMF (0.33 g, 4.5 mmol), KOAc (0.30 g, 3 mmol) and Ac_2O (2 mL) was stirred at 90°C for 2.5 h. After cooling, the precipitate was collected on a Büchner funnel and washed with H_2O/EtOH and H_2O. After drying 0.72 g (61%) of a violet solid was obtained which could be recrystallized from Ac_2O (100 mL) to give 0.50 g (42%) of red needles.

1-Butyl-5-[2-(3-ethyl-3*H*-benzoxazol-2-ylidene)ethylidene]-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (6a)

Following the procedure given above for the preparation of **5a**, reaction of **14a** (2.7 mmol) with **8a** (0.56 g, 2.7 mmol), DMF (0.30 g, 4 mmol), KOAc (0.27 g, 2.7 mmol), and Ac_2O (2 mL)afforded 0.46 g (45%) of an orange powder. Recrystallization from Ac_2O yielded 0.40 g (39%) of orange crystals.

1-Butyl-4-methyl-5-[2-(1-methyl-1*H*-pyridin-4-ylidene)ethylidene]- 2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (18)

A mixture of **8a** (2.06 g, 0.01 mol), DMF (1.1 g, 0.015 mol) and Ac_2O (4 mL) was heated at 90°C for 40 min when the mixture solidified due to the formation of **16a**. After cooling iodide **17** (1.88 g, 8 mmol) and Et_3N (1.0 g, 0.01 mol) were added and the mixture was heated at 90°C for another hour. After cooling the red precipitate was collected, washed with Et_2O and EtOH/H_2O (1:1) and dried to yield 1.4 g (54%) of a violet solid which was pure according to NMR. Recrystallization from Ac_2O gave dark-green crystals.

1-Butyl-5-[2-(1-ethyl-*1H*-quinolin-4-ylidene)ethylidene]- 4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (20)

A mixture of **8a** (1.03 g, 5 mmol), DMF (0.55 g, 7.5 mmol) and Ac_2O (4 mL) was heated at 90°C for 1 h. The mixture was cooled to 50°C and iodide **19** (1.20 g, 4 mmol) and Et_3N (0.5 g, 5 mmol) were added. After another hour at 90°C the mixture was cooled to r.t. and the precipitate was collected and washed with Et_2O and EtOH/H_2O (7:3) until the colour of the filtrate changed from violet to almost colorless. The dye was dried to yield 1.36 g (90%) of a green solid which was pure according to NMR. Recrystallization from Ac_2O gave 0.90 g (60%) of green crystals.

1-Butyl-5-[2-(1,3-diethyl-1,3-dihydro-2*H*-benzimidazol-2-yliden)ethylidene]- 2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (22)

A suspension of **16a** (0.52 g, 2 mmol) in anhyd EtOH (5 mL) was stirred under argon and **21**[23] (0.38 g, 2 mmol) was added dropwise. The mixture was stirred at 80°C for 4 h. The yellow precipitate formed was cooled to r.t., filtered and washed with EtOH (3 × 3 mL). The bright yellow solid was recrystallized from EtOH (50 mL) and dried to yield 0.40 g (49%) of **22**.

1-Butyl-2,6-dioxo-5-phenylaminomethylene-1,2,5,6-tetrahydropyridine-3-carbonitrile (24)

To a suspension of **16a** (1.30 g, 5 mmol) in anhyd EtOH (8 mL) was added dropwise **23** (0.60 g, 6.5 mmol). A yellow precipitate formed immediately and the mixture solidified. The mixture was refluxed for 2 min and allowed to cool to r.t. The yellow product was collected on a Büchner funnel, washed thoroughly with EtOH and dried in vacuo at 60°C to give 1.38 g (89%) of a bright yellow solid which exhibits intense luminescence under UV irradiation.

***N*,*N*'-Bis-(1-butyl-3-cyano-2,6-dioxo-1,2,5,6-tetrahydropyridin-5-ylidenemethylene)-*p*-phenylenediamine (26)**

A mixture of **16a** (0.52 g, 2 mmol) and **25** (0.11 g, 1 mmol) was suspended in of anhyd chlorobenzene (20 mL). During shaking, the colour of the precipitate changed from white to orange. To complete the reaction, the mixture was first stirred at r.t. for 2 h and then heated under reflux for another hour. After cooling the orange solid was filtered and thoroughly washed with EtOH to give 0.46 g (85%) of **26**. Recrystallization from DMF (30 mL), washing with EtOH and drying in vacuo at 80°C afforded 0.30 g of an intensively luminescent orange powder.

5-Dimethylaminomethylene-1,3-dimethylpyrimidine-2,4,6-trione (28)

A mixture of **27** (1.56 g, 0.01 mol), DMF (1.1 g, 0.015 mol) and Ac_2O (5 mL) was heated at 90°C for 2 h. After cooling to r.t., the liquid was triturated with Et_2O (5 mL) to give almost colorless crystals during standing for 2 h. The crystals were filtered and washed with Et_2O (3 × 4 mL) and dried in vacuo at 40°C to yield 1.60 g (76%) of **28**; mp 107–108°C (Lit.[22] mp 109°C).

^{1}H NMR (200MHz, $CDCl_3$/TMS, 25°C): δ = 8.14 (s, 1 H, met-H), 3.42 (s, 3 H, NCH_3), 3.38 (s, 3 H, NCH_3), 3.31 (s, 6 H, barb–NCH_3).

5-(2-Dibutylamino-4-phenylthiazol-5-ylmethylene)- 1,3-dimethylpyrimidine-2,4,6-trione (29)

A mixture of **27** (1.56 g, 0.01 mol), DMF (1.1 g, 0.015 mol) and Ac_2O (4 mL) was heated at 90°C for 1 h. Compound **11a** (3.6 g, 0.01 mol of 80% purity) was added to the pale-yellow solution and the mixture was stirred at 90°C for another 2 h. The solid which precipitated on cooling, was collected, washed with *i*-PrOH and EtOH/H_2O (8:2), and dried to give 3.0 g (66%) of an orange dye which was pure according to NMR. Recrystallization from toluene yielded 2.7 g (59%) of orange crystals. If the reaction was carried out with all components mixed together (General Procedure B, see above) a yield of only 40% was obtained.

5-[2-(1,3-Dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)-ethylidene]-1,3-dimethylpyrimidine-2,4,6-trione (30)

Reaction was carried out as described for **29** staring from **27** (1.56 g, 0.01 mol), DMF (1.1 g, 0.015 mol) Ac_2O (4 mL) and **12a** (1.73 g, 0.01 mol) to give 3.20 g (94%) of a luminescent orange solid. If the reaction was carried out with all components mixed together (General Procedure B, see above) a yield of only 3% was obtained.

1,3-Dimethyl-5-[2-(1-methyl-1*H*-pyridin-4-ylidene)ethylidene]-pyrimidine-2,4,6-trione (31)

A mixture of **27** (1.56 g, 0.01 mol), DMF (1.1 g, 0.015 mol) and Ac_2O (4 mL) was heated at 90°C for 1 h to give a pale yellow solution. To this solution were added **17** (1.88 g, 0.008 mol) and Et_3N (0.8 g, 0.008 mol) added and the mixture was stirred at 90°C for another 2 h. The solid which precipitated on cooling was collected, washed with Et_2O and EtOH/H_2O (7:3) and dried to give 0.20 g (9%) of an orange dye which was pure according to NMR. Recrystallization from AcOH gave orange crystals.

5-[2-(1,3-Dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)-ethylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione (33)

Reaction was carried out as described for **29** starting from **32** (1.44 g, 0.01 mol), DMF (1.1 g, 0.015 mol), Ac_2O (4 mL) and **12a** (1.73 g, 0.01 mol) to afford 1.08 g (33%) of a red solid.

Attempted Synthesis of Dye 36

A mixture of **34** (1.01 g, 4 mmol), DMF (0.45 g, 6 mmol) and Ac_2O (2 mL) was heated at 90°C for 2 h to give the enamine **35** which precipitated on cooling as a yellow solid. Addition of **12a** (0.64 g, 3.7 mmol) and heating for another 2 h at 90°C afforded after cooling, filtration and washing 1.1 g of an orange solid which was composed of 60 mol% enamine **35**[26] and 40 mol% dye **36**[13b] according to ^{1}H NMR and MS (EI) characterization. The major product in the mother liquor was indoline **15** according to TLC and ^{1}H NMR analysis.

1-Butyl-5-(3-dimethylaminoallylidene)-4-methyl-2,6-dioxo-1,2,5,6-tetrahydropyridine-3-carbonitrile (38)

A mixture of **8a** (2.06 g, 0.01 mol), **37** (0.99 g, 0.01 mol) and Ac_2O (5 mL) was stirred at 90°C for 2 h. The precipitate which formed upon cooling was collected on a Büchner funnel and washed with *i*-PrOH to give after drying 2.58 g (90%) of a yellow dye. Recrystallization from EtOH gave luminescent yellow needles. The same product was isolated in 85% yield in the presence of 0.01 mol thiazole **11a**.

MS (EI): *m*/*z* (%) = 287 (100), 270 (85), 187 (98).

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